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The Metallurgist.

Supplement to The Engineer, *June, 1933.*

Gases and Shrinkage.

IN recent years increasing attention has been given, particularly in regard to the non-ferrous metals, and among those more especially the aluminium alloys, to methods for the removal of dissolved gases prior to or during the casting process. This activity has been due to the recognition of the deteriorating effect which the presence of numerous gas bubbles has upon the mechanical qualities of these materials. As the result of the methods which have been developed and of the attention which has been called to the whole subject, the standard of castings in regard to soundness and freedom from minute bubbles known as "pin holes," especially in the case of aluminium, has improved to a very marked extent of late. Of the general advantage of this improvement there can, we think, be little doubt, since it has brought with it not only a better standard of surface finish, but also, more especially in those alloys which attain a high degree of strength after heat treatment, a very definite increase in strength. Beyond this it is realised that qualities which cannot be readily measured by a simple test or included in a specification are appreciably affected by the presence or absence of gas. It is quite clear that the absence of "pin holes" in a machined surface subjected to wear, such as the skirt of a piston, will make for better durability both of the casting itself and of the metal with which it comes into contact. "Pin holes" and porosity cannot fail to initiate local erosion and wear, as they are apt to serve as reservoirs for abrasive material derived either from the alloy itself or from outside.

The problem of gases and their removal, however, is by no means a new one, nor is it confined to the non-ferrous metals and alloys. In steel it has been familiar for many years, and the controversy as to the admissibility of "rimming" steel for certain purposes as against steel derived from piped ingots is an old one. The use of "rimming" steel has persisted for many purposes in spite of the severe criticism which has been levelled against it by many technical and scientific men of high standing. This is an economic question because certain grades of steel can only be produced at the very low price which is demanded for commercial purposes if a "rimming" ingot is employed. The discard required for the elimination of pipe, even when a large feeding dozzle is used, is too great for steel of this type. Further, it is claimed that blow-holes in "rimming" steel, provided that they do not lie too near the surface of the ingot, are subsequently welded during the rolling operations. While there are many who doubt the validity of this view, steel made in this manner is still very widely produced and used. We do not propose to enter further at this point into this particular question, since it is a large one which has been widely discussed. The nature and use of "rimming" steel, however, serves as an example in which the presence of gas in a solidifying metal is not only regarded as unobjectionable, but is actually relied upon to counteract the large amount of shrinkage which would otherwise occur. In the case of steel, this is done consciously and an attempt is made to justify it by arguments which have been indicated above. There can be no doubt, however, that in a great many castings produced from commercial alloys the gas content must play a similar part. Provided that the gas is evolved in sufficiently minute bubbles to be widely scattered throughout the metal, its presence may not be particularly noticeable on the machined surfaces of such a casting. From the point of view of ease of production, where a large amount of shrinkage introduces certain difficulties from the occurrence of "draws" and cavities, a certain gas content is obviously very useful. It has, in fact, been discovered that when aluminium alloys are thoroughly freed from gas by one of the various methods now available, the result is a material which shows what the foundry describes as "excessive shrinkage" and difficulty is experienced in making satisfactory castings with it. It is not unnatural that the remedy of leaving a certain amount of gas in the material is advocated and used in many quarters. The point we wish to raise, however, is whether it is wise to employ such a remedy, since it seems that the finished casting is, in reality, appreciably porous and that it cannot possess the properties of strength and durability of which the alloy in the truly solid state is capable. It will, of course, be said that castings made in this way have been used for a long time and have given satisfaction. The fact that they have been thus used, cannot be denied, but the degree of satisfaction which they have given is more difficult to ascertain, and it would not be safe to argue that because they have given some degree of satisfaction in the past therefore they will meet the requirements of to-day and of the future. It will only be necessary for some competing firm, either in this country or abroad, to break away from the traditional use of gas as a counterpoise to natural shrinkage in order to demonstrate to users that better castings can be commercially produced. When this has been done, as it has been done to a large extent in many aluminium alloys, all foundries will have to follow if they do not wish their products to be outclassed.

Nor must it be supposed that the difficulties to be overcome on account of what is described as "excessive shrinkage" of gas-free metals are by any means insuperable. It is true that many existing methods of moulding, gating, and feeding castings

will not answer with metal of this type. Such difficulties, however, have frequently been encountered in the past when new alloys have been brought forward to meet new requirements. More than once the foundry industry has almost unanimously exclaimed that the alloy could not be cast and in many cases the reason given has been "excessive shrinkage." The well-known "Y" alloy, among the light aluminium alloys, was a striking example of this kind and its development was delayed for many years for this reason. It was only when a few of the more enterprising founders developed methods which made it possible to produce sound castings in this material that its development took place. It seems very possible that a similar course of events will follow in regard to gas-free alloys and their relatively greater shrinkage. Methods of casting which overcome this difficulty will have to be developed and adopted, in spite of the fact that at the moment the use of material containing a considerable amount of gas appears to offer the easier solution.

International Standards.

WE understand that the question whether Great Britain shall join the International Standards Association (I.S.A.), even as an associate member, is again under discussion, and that objections to such a course are being raised in certain quarters. We fully realise the difficulties and pitfalls which inevitably beset attempts at international standardisation, but it must be remembered that these vary widely, according to the nature of the standards in question. The dimensional standardisation of mechanical parts is a matter of peculiar difficulty, so far as this country is concerned, on account of the difference between the metrical units employed on the Continent and in America and our British system. Yet this is a difficulty which manufacturers in this country who desire to cater for Continental markets must inevitably face, and the adoption of an international standard, so far as countries employing the metric system are concerned, is not likely to be in the slightest degree hindered or prevented by the abstinence of British manufacturers. Where standards relating to materials are concerned, the position is probably not so difficult, although there are still many obstacles to be overcome.

There is a natural tendency, in arriving at international standards, for each country to seek advantages from its own point of view, which usually entail corresponding disadvantages to other competing countries. This is, of course, a difficulty which applies to international understandings of all kinds, but we are coming to realise, in the political sphere, that such understandings must be arrived at if the future progress of the world is to be assured, and we would strongly urge that a similar spirit of compromise and mutual adjustment should also be adopted in the industrial and especially in the technical world. If the Economic Conference of London is to be successful, that spirit of compromise will have to govern the decisions arrived at, and it would be unfortunate to find technology lagging behind in such a matter. Quite apart from this general question of international attitude, however, there is much to be gained by British representation on and participation in the work of an important international standardising body. Failure to be represented there or any excessively uncompromising attitude is likely to be interpreted by the representatives of other nations in a sense very unfavourable to the manufacturers and technologists of this country. A spirit of aloofness and superiority will not be tolerated, and is most unlikely to lead to an attitude of confidence and friendship towards our industries abroad. Yet it is this goodwill and appreciation of the capacity of this country to furnish the best that can be obtained in the world upon which our foreign trade in technological matters must depend. If we cannot supply goods at prices below those of our foreign competitors, we can only hope to obtain business by securing the highest measure of confidence. It is in securing this confidence that our adequate and cordial participation in these international activities is so important.

Even if we accept the general principles advocated above, it still remains an open question whether participation, wholly or in part, in the I.S.A. in its present form is desirable. Here, we think it quite likely that the present organisation of that body leaves much to be desired. Standardisation of any kind can only be undertaken successfully if certain fundamental principles are observed. These are essentially two. The first is the proper and proportionate representation on committees undertaking standardising work of those interested or concerned and of those only. Manufacturers, users, and technologists directly interested in a particular product which is under consideration are all required to give their aid in arriving at sound standards, and the varying standpoints of these three groups should be adequately and proportionately represented, while the committee should be kept free of others who are not directly concerned. This becomes more important when representation is international, because there is a tendency for every country to desire to be represented on every occasion, even when its own interests or products are only concerned to a very minor degree.

The second principle is that majority decisions should never be taken, but that standards can only be arrived at by unanimous consent. This is more important in the international sphere than it is in purely national standardisation, because it will never do to allow a majority of those interested to impose their will upon a minority whose interests may suffer severely in consequence. If and where satisfactory international standardisation is possible, then and there unanimous consent to such standards is obtainable. Where this is not the case, it is clear that there are either conflicting views or conflicting interests which have not yet been reconciled, and that therefore an attempt at international standardisation is premature.

In view of these considerations, it seems quite possible that the existing organisation of the I.S.A. may not be entirely satisfactory, but we would suggest that this is not a reason for standing aloof from it, but rather for taking an active part in it and seeking and securing any necessary modification of its organisation, so as to conform to the principles which are, we think, logically necessary for the functioning of such a body. We have seen in the case of the International Association for Testing Materials, whose activities are entirely distinct from and yet related to those of the I.S.A., a very ready acceptance of sound and logical principles of organisation when these are put forward in a reasonable and convincing manner, and we do not doubt that similar counsels will prevail for the I.S.A., provided that full British support be given.

Inverse Segregation.

By H. SUTTON, M.Sc.

No. II. (*continued from April issue*).

THE recent work of Haase[9] on volume changes caused by diffusion in metallic alloys draws attention to the importance of these changes in relation to inverse segregation as indicated by the earlier work of Jokibe. Haase made copper-zinc alloys containing 2, 10, 15, 23 and 37 per cent. of copper and cast the alloys in chill moulds giving billets 20 mm. diameter and 200 mm. long. The billets were cut into pieces 20 mm. thick, and the densities of the pieces were determined. The pieces were then heated in a furnace the temperature of which was raised progressively. At chosen intervals samples were quenched and the quenched samples weighed in water to determine their density. During this operation the specimens increased in weight, on account of absorption of water by the samples, most of which had been rendered porous by the heat-treatment. The alloys containing 2 and 37 per cent. of copper showed little or no density change after reheating. The density of the 10 per cent. copper alloy increased with increasing tempering temperature at first, but decreased when the solidus temperature was exceeded. With 15 per cent. of copper, the decrease in density is greatest and almost the same for all temperatures of reheating, while with 23 per cent. of copper considerable decrease in density was first observed after quenching above the solidus line. Owing to difficulty in determining accurately the densities of the expanded alloys, observations on changes in length were made in subsequent experiments, the ends of the specimens in the same alloys being machined flat and parallel. The specimens were in this case tempered at constant temperature for periods up to one week and afterwards cooled in air. With alloys containing 10 and 23 per cent. of copper, reheating to low temperatures caused a decrease in length, the considerable increase in length being first observed after reheating to temperatures in the vicinity of the solidus. In the alloy containing 15 per cent. of copper, which also showed the highest value of expansion in Jokibe's experiments, the increase in length had begun already at 250 deg. Cent. and attained a value of 13·5 per cent. at the solidus temperature. The shape of the specimens reheated to 500 deg. Cent. for twenty-four hours underwent considerable changes. While the diameter of the cylinders increased uniformly, the end-faces became concave. This change is the opposite to that observed by Masing and Overlach[10] in antimony-bismuth alloys, where a convex shape was developed on the ends of cylindrical specimens of similar dimensions. Microscopic examination of reheated specimens showed martensite-like banding in the zinc-rich γ-constituent, an indication of breakdown of super-saturated solid solutions. In the transverse sections inverse segregation could be seen clearly.

Levelling up of the differences in concentration of copper originally present in the specimens takes place on reheating, but the rate at which this proceeds is very slow. After seventy-two hours at 500 deg. Cent. the differences in a particular specimen were reduced by half.

Haase mentions that volume changes of the same kind as observed by him in the copper-zinc alloys on reheating are shown by vacuum-melted antimony-bismuth alloys. This fact and the observations of Bohner on practically gas-free aluminium-copper alloy render it very improbable that gas-evolution can be a leading factor in segregation phenomena in general. There appears no ground for assuming that a transformation is concerned in the volume changes observed in the copper-zinc alloys.

Haase concludes that diffusion remains as the only possible cause of the volume changes in the copper-zinc alloys and the similar effects observed by Masing[11] in antimony-bismuth alloys. If a great difference exists in mobility of the atoms of the two constituents, which appears probable in both the copper-zinc and antimony-bismuth alloys, a marked increase in size of the dendritic crystals and in the formation of cavities by the pressing of the growing dendrites one upon the other may well be imagined to arise from a directional diffusion. If a relationship exists between the observed increases in dimensions and segregation, as appears probable in view of the parallelism between the two effects shown by Jokibe, segregation would be expected to occur also in the antimony-bismuth alloys. Haase shows that this is the case; a chill cast billet 20 mm. diameter and 200 mm. long showed normal segregation in varying degree from top to a maximum at the bottom. Haase suggests that normal and inverse segregation are not fundamentally different phenomena and the work of Bohner appears to the writer to support that view. In some billets described by Haase inverse segregation occurred at the top and normal segregation at the bottom.

Haase explains the difference in changes in shape shown by the copper-zinc and antimony-bismuth alloys respectively, by the different form of the segregation in the two cases. The greatest volume increase takes place in the zone in which the constituent possessing the greatest diffusibility is most abundant. Hence the porosity is greatest at the surface in the copper-zinc alloys and in the middle in antimony-bismuth alloys.

According to Haase, when these alloys are cast in chill moulds, primary dendrites separate first at the chill wall and in the case of copper-zinc alloys there very soon forms a skull of crystals adhering to one another. Simultaneously with the deposition of primary dendrites, the diffusion of zinc atoms from the melt into the copper-rich dendrites commences. This diffusion is associated with the formation of cavities, and into these the zinc-rich liquid from the centre flows, the flow being maintained as casting proceeds. While copper-zinc alloys can be heated to temperatures just below the liquidus for a short time without undergoing marked changes in shape, an alloy of 75 per cent. bismuth, 25 per cent. antimony, apparently melts at a temperature of about 100 deg. below the liquidus point. From this it may be concluded that in the latter alloy, formation of a strong skull of primary dendrites first occurs at temperatures only a little above the solidus point. Since the temperature in the centre is higher than in the zone next to the chill-mould, in this case diffusion can occur more vigorously there than near the surface, so that a movement of the mother liquor from the outside to the inside occurs, *i.e.*, normal segregation. In addition to the habit of the primary dendrites, the temperature-fall between outside and inside determines the form of the segregation, whether normal or inverse. Following this explanation of

[9] Haase, Zeits. für Metallk., Oct., 1932, pp. 258–261.

[10] Masing and Overlach, Wiss. Veröff. Siemenskonzern, Bd. 9 (1930), p. 331.

[11] Masing, Zeits. für Metallk., Bd. 17 (1925), p. 261.

segregation effects, Haase refers to effects observed in industry, but not hitherto explained. In the case of zinc-base die castings, which contain about 4 per cent. of copper with rather more tin or aluminium, Haase regards the volume changes observed as definitely attributable to balancing up of composition by diffusion. The volume changes occur at room temperature in rather long periods of time with the same features—first a decrease and then later an increase in length—as those observed by Haase in pure copper-zinc alloys at higher temperatures. Also the well-known expansion of dental amalgams, for which no basis can be found in the constitution of the alloys, can be explained in the same way by diffusion effects within the alloys in the direction of attainment of equilibrium.

The phenomenon of inverse segregation in silver-copper alloys has been studied recently by Watson,[12] who finds that the first-formed primary crystals are free to move under the influence of gravity when the alloy is maintained for sufficient time at temperatures between liquidus and solidus, but that the primaries which have segregated under the influence of gravity are apparently repelled from their position by the application of severe local chilling to their vicinity. All the effects of "liquation" and inverse segregation observed in these alloys in ordinary practice are attributed to the formation of primary crystals at the chilling surfaces of moulds and between the temperatures corresponding with the "liquidus" and "solidus," followed by their immediate migration towards the hotter portions of the mass. In the copper-silver alloys the separation of the copper-rich and silver-rich solid solutions from the liquid alloys during slow cooling are accompanied by migration of the primary crystals to the top or bottom under the influence of gravity. While the results published in this valuable paper appear fully to justify the conclusions reached in a technical sense, it appears that it has yet to be proved that definite translation of primary crystals occurs. The writer would suggest tentatively that when a pot containing liquid alloy and solid primary crystals which have migrated to top or bottom at a temperature just below the liquidus, is suddenly cooled from the end opposite to that at which the primary crystals have already collected under the influence of gravity, fresh primary crystals will tend to separate at the cooled surface. These enrich the residual liquid in the other constituent and render it capable, at the higher temperatures of parts remote from the cooled end, of re-dissolving some of the primary crystals originally present there, before final solidification occurs. If the possibility is entertained of absorption of the lower-melting constituent, *i.e.*, the eutectic, by the primary zone near the cooled face, during the later stages of freezing as is now assumed by most investigators of the subject, the results obtained appear to present similar features to those of other workers in this field.

The problem of the mechanism of inverse segregation cannot yet be said to have been in any way settled, but the researches here mentioned, although only a few of the many studies of the subject, provide valuable guidance for future investigations. Further careful work is needed to identify the changes which result in the various forms of segregation in cast alloys, but the work that has already been done has aided industry to produce castings with a chemical composition as uniform as possible throughout their mass.

[12] Watson, "Proc.," Inst. Met., Vol. XLIX., pp. 347–358.

Recovery of Steel after Fatigue Testing.

By R. A. STEPHEN, M.Sc., and W. R. D. JONES, D.Sc.[1]

DURING solidification and cooling of a steel casting in a sand mould, the crystal grains are subjected to severe internal strains due to the cooling stresses. This results in a Laue pattern, the spots of which are never perfectly round, but are drawn out and distorted. A large number of Laue photographs of steel castings[2] have been taken by the authors,[3] both in the "as cast" and in the annealed conditions. Radial asterism, indicative of internal strain, is still

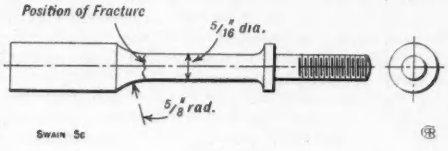


FIG. 1

found to be present after annealing for four hours at 875 deg. Cent.[4]

It is known that the surface of a fatigue fracture usually exhibits two definite zones—a smooth and a coarse part (see Fig. 2). Once a crack has originated, the applied stress is concentrated and propagates the crack which spreads until the cross section of the material is so reduced that the remaining portion tears away with great rapidity. The smooth zone is that through which the crack passes, and the coarse

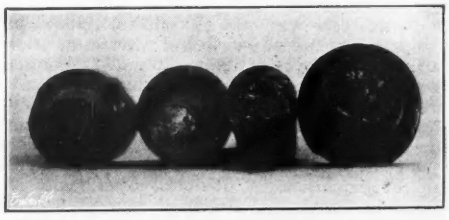


FIG. 2—*Fatigue Fractures. Wöhler Test Piece. Motor Cycle Spindle Fractured in Service.*

is the portion torn away in the final rupture. As a rule, the Laue patterns obtained from several ex-

[1] Department of Metallurgy, University College, Cardiff.

[2] The chemical analysis of the steel castings was :—Carbon, 0·32 per cent.; silicon, 0·37 per cent.; manganese, 0·67 per cent.; sulphur, 0·041 per cent.; phosphorus, 0·024 per cent.

[3] For this purpose a specially designed X-ray tube, with a tungsten anti-cathode operating at 70,000 volts, was used to direct intense beams through three cylindrical channels (about 0·5 mm. diameter) in a mass of brass. This permitted three specimen slips of steel to be photographed simultaneously. The slips were cut sufficiently thick to ensure that the process of sawing did not interfere with the structure of the final slip, which was to be subjected to X-ray examination. The thickness of the slip was reduced by a combined grinding and etching process, carried out simultaneously—the etching reagent acting as a lubricant during the gentle grinding. By this means thin slips, 0·02 cm. in thickness, were prepared without straining the specimens.

[4] The fatigue tests were carried out with a Wöhler type machine running at 2300 r.p.m. The form of the test pieces is shown in Fig. 1. The line of action of the load was 2in. from the neck, and its value was calculated from $f = M/Z$, when M = bending moment, Z = section modulus. As a rule, specimens fractured at the neck.

posures through either zone of fractured fatigue test pieces showed only radial asterism. X-ray and microscopical examination of drawn or rolled metallic aggregates has shown definitely that the crystal grains of which the aggregate is composed

FIG. 3—*Laue Photograph of Fractured Fatigue Test Piece of Steel in the "As Cast" condition 10 months after Fracture.*

FIG. 4—*Laue Photograph of Fractured Fatigue Test Piece of Steel which had been Annealed at 875° C. for 1 hour 10 months after Fracture.*

orient themselves so that their axes tend to lie in one direction. In the coarse zone of a fractured fatigue specimen a preferred orientation of this type is to be expected, and its presence is manifested by the

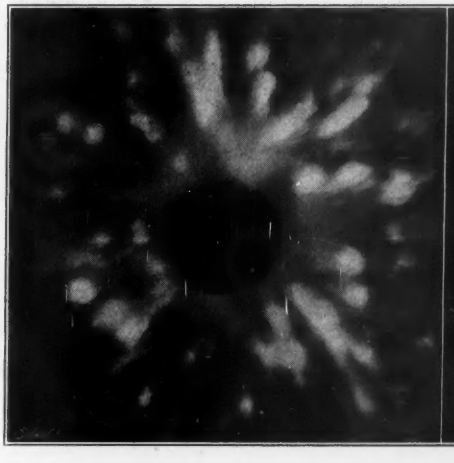


FIG. 5—*Laue Photograph of Steel in the "As Cast" condition before Mechanical Testing.*

appearance of the typical star pattern in the corresponding Laue photograph.

Fig. 5 is typical of the Laue patterns of the steel in the "as-cast" condition (which had not been subjected to any artificial mechanical stresses). The large grains of the cast steel which are subjected to stresses during cooling from the molten state give rise to the "streaky" pattern. Fig. 6 is a photograph taken after annealing for one hour at 875 deg. Cent.,[5] no individual Laue spots can be detected, the grain size is small owing to recrystallisation, and no large crystal grain is present. Fig. 7 is typical of the general appearance of the Laue pattern of the steel near the fracture taken as soon as possible after the test in the fatigue testing machine, and

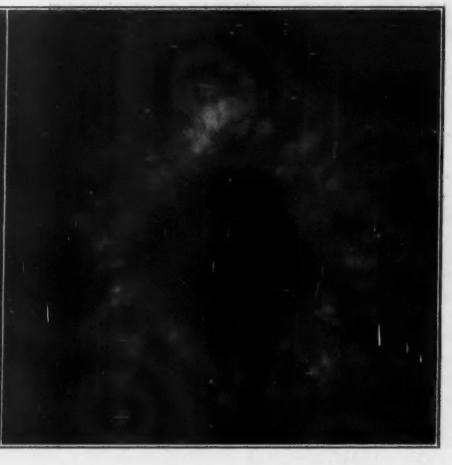


FIG. 6—*Laue Photograyh of Steel which had been Annealed at 875° C. for 1 hour before Mechanical Testing.*

shows the distorted and strained state of the grains.

A number of fatigue test pieces were examined about ten months after fracture in the testing machine.

[5] For steel castings of this type the commercial practice is to anneal at 875 deg. Cent. for one hour per inch cross-section—Jones and Foster, S.W. Inst. E., 1932, XLVIII.

During the interval they had been kept in a box at ordinary temperature (not in the proximity of any radiator). Out of a large number of Laue photographs taken through the coarse zone of the fracture, two presented unusual features. These are shown in Figs. 3 and 4. In spite of the distortion shown by the rest of the pattern, a number of perfect undistorted Laue spots can be readily seen in Fig. 3. Round and undistorted spots, although less clear, are also quite definitely present in Fig. 4. At least one unstrained crystal must have been present in the path of the beam of X-rays in both cases. Although the large, perfectly round Laue spots seen in Fig. 4 indicate a grain size comparable with that of the cast steel, the Laue pattern of the steel after annealing, but before testing, shows a fine-grained structure which is seen in Fig. 6. These large unstrained crystal grains must either have developed during or subsequent to the testing operation. The hypothesis that they developed during the testing process cannot be supported. It is not probable, even if such large unstrained grains had existed prior

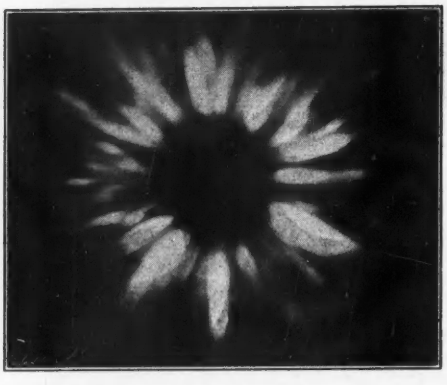


FIG. 7—*Laue Photograph typical of the General Appearance of Fractured Fatigue Test Piece of Steel immediately after Fracture.*

to the testing, that they would have remained undisturbed after so many reversals of stress—remembering that the slip of steel examined was taken as close as possible to the region of fracture. The only acceptable explanation of their presence is that the unstrained grains developed during the interval that elapsed between the stressing of the specimen and the X-ray examination. A clue to the explanation of their origin arises from the fact that these perfect Laue spots were observed only in the coarse zone of the fracture—where the grains had first been strained by the reversed stresses and then by the final rupture which is almost of a tensile nature.

The potential energy content of crystals is higher in the strained than in the unstrained condition, and hence it is to be expected, as pointed out by Polanyi,[6] that under suitable conditions a spontaneous return to the unstrained state may take place. In the case of single crystals, this is termed "recovery." In the polycrystalline aggregate examined, relief of stress has occurred, and the conditions in the coarse zone of the fractured test pieces are evidently favourable for grain growth.

Since the normal grain size of the steel in the "as-cast" condition is larger, and, if freed from strain, would have given rise to a Laue spot comparable in size with those seen in Fig. 3, there may be some doubt that a new grain has developed from the coalescence of "recovered" small grains. Fortunately, Fig. 4, in which large Laue spots are also visible, helps to decide the question, as coalescence of similarly oriented grains has occurred. (The Laue pattern before testing showed a fine-grained structure—Fig. 6—in which a large grain did not exist.) It seems that a process similar to that of "recovery," as observed in the case of single crystals, has taken place in the polycrystalline aggregates tested.

[6] "Trans.," Far. Soc., 1928, 24, 80.

SUMMARY.

Laue pinhole diagrams have been obtained from slips cut from broken fatigue test pieces. Large undeformed Laue spots have been observed in photographs taken through the coarse zone of the fracture, ten months after testing in a Wöhler type machine. These have been interpreted as indicating that large unstrained grains have developed subsequent to fracture, and relief of stress accompanied by grain growth at normal temperature has taken place; that is to say, the X-ray analyses point to the existence of a process of "recovery" at ordinary temperatures in the case of a polycrystalline aggregate, previously subjected to stress of a particular kind.

The X-ray examination was carried out in the Viriamu Jones Research Laboratory of the Physics Department of University College, Cardiff, and cordial thanks are due to Professor R. T. Dunbar for his valuable help and for the use of the laboratory.

Electro-deposition of Zinc.

THE electro-deposition of zinc from sulphate solutions is largely influenced by the purity of the electrolyte and when, as in the case of electrolytic recovery of the metal from leached ores, impurities are being continuously taken up, chemical control of the electrolyte becomes vital to the success of the process. P. Röntgen and R. Buchkremer have

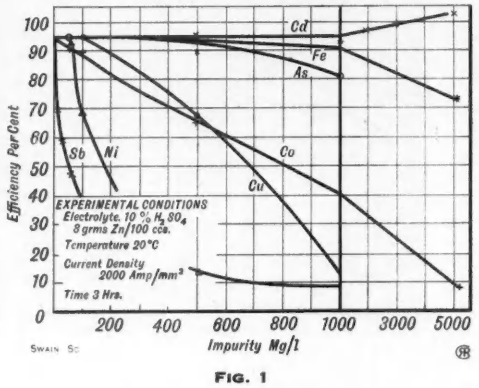


FIG. 1

recently carried out an investigation* at the Technical Hochschule, Aachen, which follows up earlier work of their own and which adds considerably to the available information on this subject. The authors have carried out their tests on a number of the

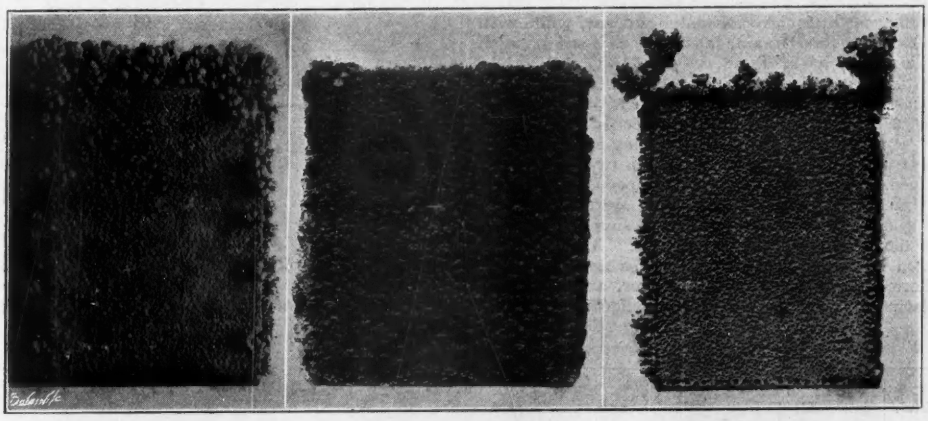
* P. Röntgen and R. Buchkremer, *Metall und Erz*, November, 1932.

impurities most commonly met with in practice, taking them singly, and have used electrolytes containing sulphuric acid alone, as well as acid zinc sulphate solutions of varying acid and metal content. In their experience anodes of lead gave electrical results interchangeable with those of platinum, and both kinds of anode were used in their experiments.

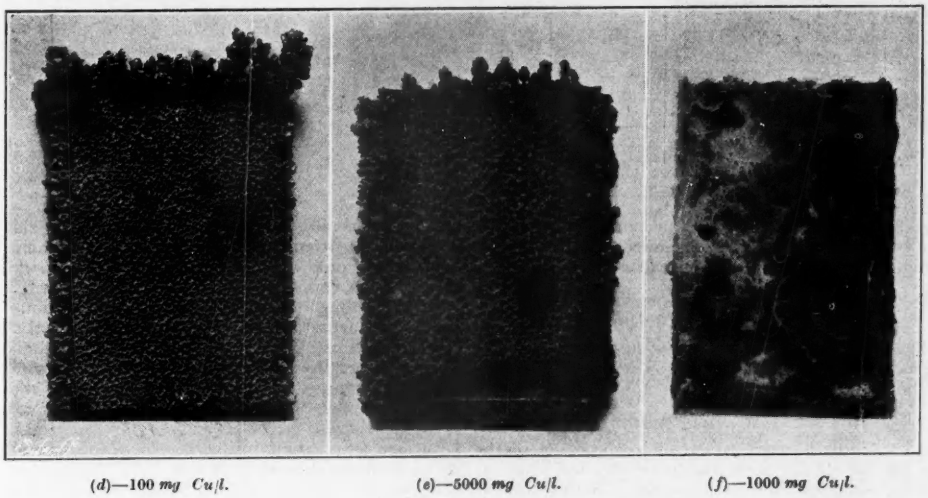
INFLUENCE OF IMPURITIES ON CURRENT EFFICIENCY.

The effect of impurities is, as Fig. 1 shows, in general to lower the current efficiency. Among the metals tested antimony has the most seriously harmful influence, while cadmium apparently causes an increase in the efficiency. This is because cadmium, which is deposited with the zinc, has a higher atomic weight (Cd := 112·4, Zn : 65·4). The adverse influence of antimony increases rapidly with acidity, but is reduced by the presence of a colloid such as gelatine, which, however, has itself a slightly adverse effect on the efficiency in electrolytes free from antimony.

In view of the general use of lead anodes in commercial working the effect of lead as an impurity was specially observed and a very interesting fact noticed. Speaking generally, lead anodes give a higher current efficiency than platinum, so long as the anode is not shielded by a diaphragm or the solution allowed to become saturated with lead sulphate. This effect is particularly marked when antimony is present as an impurity in the electrolyte, which leads the authors to advance the suggestion that lead peroxide in colloidal suspension may act in the same manner as gelatine.



(*a*)—1000 *mg Cd/l.* (*b*)—5000 *mg Cd/l.* (*c*)—1000 *mg As/l.*



(*d*)—100 *mg Cu/l.* (*e*)—5000 *mg Cu/l.* (*f*)—1000 *mg Cu/l.*

FIG. 2

INFLUENCE OF IMPURITIES ON THE PHYSICAL CONDITION OF THE DEPOSITS.

As long as the current efficiency remains above 90 per cent. (or, in the case of cadmium, remains below 95 per cent.) the deposit has the normal granular appearance. Once these values are passed, however, a characteristic change is observed, which is clearly shown in the illustrations, Figs. 2 and 4. Iron can be

present up to 5000 milligrammes per litre before corrosion patches appear on the cathode, the only effect of lesser concentrations being to lower the current efficiency by the energy absorbed in the alternate oxidation and reduction at anode and cathode. Cadmium, as is shown in Figs. 2 *a* and *b*, causes nodules to form all over the face of the cathode. Arsenic, Fig. 2 *c*, produces growths like buds and does not, as is generally suggested in the literature of the subject, cause corrosion.

Copper has no adverse influence when present up to 100 milligrammes per litre (Fig. 2 *d*). With 500 mg. per litre corrosion patches occur, while with 1000 mg. per litre the zinc falls away as it is deposited, and is re-dissolved (Figs. 2, *d*, *e* and *f*.)

Nickel causes severe corrosion, which becomes progressively worse as the concentration is raised. Figs. 3, *a*, *b* and *c* show how the corrosion is noticed first at the edges, but, with increasing concentration, starts at many points and spreads over the whole surface. This type of corrosion is peculiar to cobalt and nickel. In Fig. 3 *c* the white spots and bands are the bare aluminium cathode showing through the dark ground of spongy zinc. Antimony, as shown in Figs. 3, *d*, *e* and *f*, causes nodular, badly adherent deposits without, however, any corrosion. Gelatine much reduces the evil effects as seen in Figs 3, *g*, *h* and *i*. The best proportion of gelatine lies between 0·5 and 1·0 grammes per litre, 2·0 being, as illustration 18 shows, excessive.

current increases with rising voltage. In the curves for the electrolyte containing zinc, there are two arrests, the first corresponding with the hydrogen over-voltage, as in the previous case, the second with

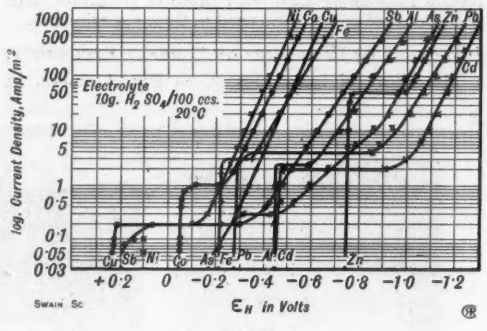


FIG. 3

the deposition of zinc on the particular impurity-metal as cathode. This second figure is the important one, as it is clear that, unless the current density is higher than the zinc deposition point, no zinc can be deposited on this impurity. With anything less, hydrogen only will be liberated, the cathode will receive no deposit, and current efficiency will suffer by the amount wasted in hydrogen production. This critical current density, which varies greatly with different impurities, must be passed if satisfactory deposition is to be obtained. The authors emphasise the importance of estimating this figure on the true surface area. The deposit always becomes rougher as deposition proceeds, and thus increases the surface area, calling for increased current to maintain the current density. It will be noticed that the curves (Fig. 3) are all approximately parallel above the point where hydrogen begins to be given off, and this leads the authors to conclude that in the equation representing these curves potential$=a+b$ log. current density, the value of b is the same for all the metals.†

The antimony curve is abnormal owing to the property this metal possesses of forming a surface

TABLE I.

Metal.	Equilibrium potential.	Milligrammes impurity per litre.						
		1.	10.	50.	100.	500.	1000.	5000.
Zn ..	−0·76							Slight
Fe ..	−0·43	—	—	—	—	—	—	trace
Cd ..	−0·40	—	—	—	—	—	0·3 (1·17%)	3·2 (12·4%)
Co ..	−0·29	—	—	—	Very slight trace			
Ni ..	−0·23	—	—	0·007 (0·039%)		0·13 (5·56%)		
Pb ..	−0·13			Not estimated in electrolyte				
Sb ..	+0·16	Trace	Trace					
As ..	+0·30	,,	,,					
Cu ..	+0·34	,,	,,	Trace	0·04 0·225%	0·26 7·48%		

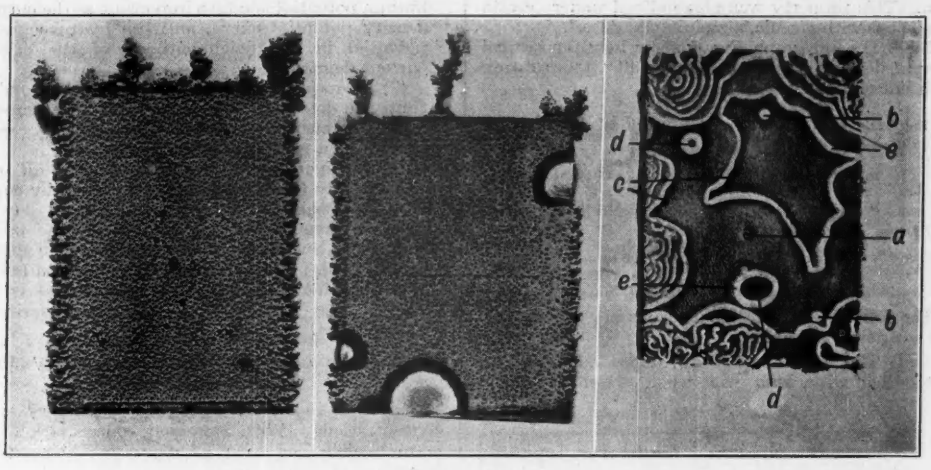
INFLUENCE OF IMPURITIES ON THE CHEMICAL CONSTITUTION OF THE DEPOSIT.

The attached Table I. shows the amount of impurity deposited with the zinc for various concentrations of the impurity.

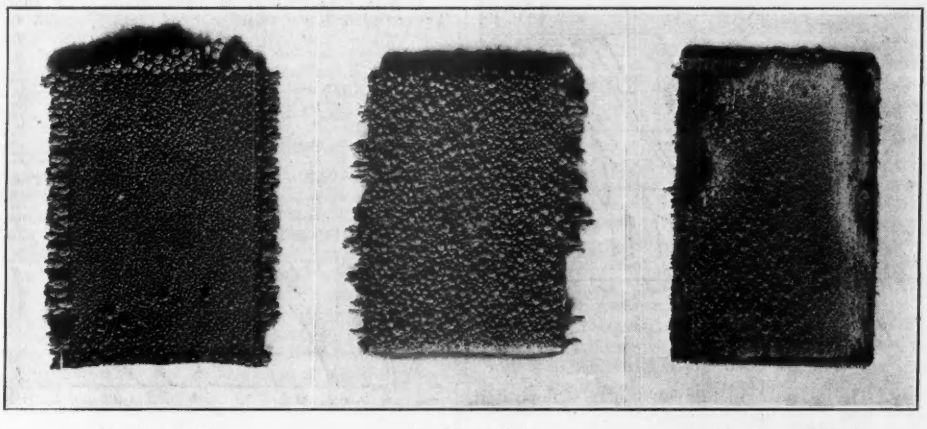
POTENTIAL MEASUREMENTS.

An attempt is made to correlate the effect of the various impurities with the potential for different current densities. For the experiment both sulphuric acid alone (10 grammes per litre) and sulphuric acid with zinc sulphate (10g H_2SO_4 per litre, 8g $ZnSO_4$ per litre) were used with anodes of platinum or lead. Cathodes were made of the particular impurity under test, and the results are shown in the graphs Figs. 3 and 5, on which log current-density is plotted against anode-cathode potential. Following the curves for plain sulphuric acid an arrest is found at a point where, with the building up of the hydrogen film on the cathode face, the voltage is raised without any increase in the current flowing. When the point corresponding with the hydrogen over-voltage figure is reached, hydrogen is liberated as bubbles and the

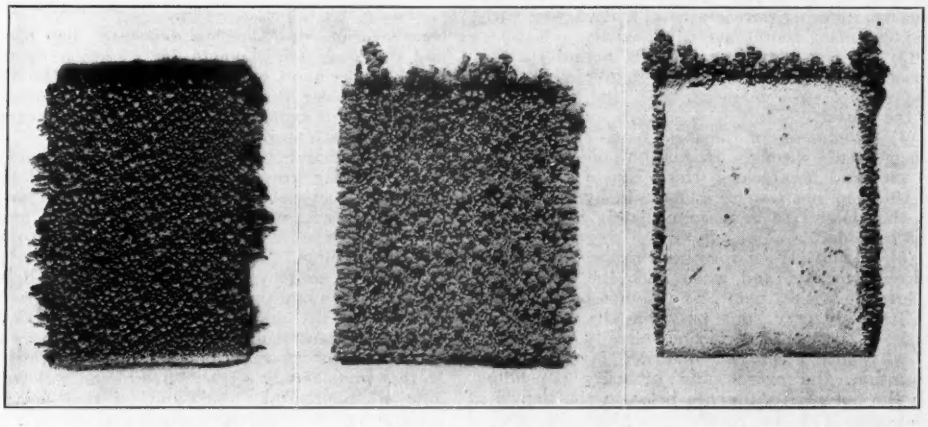
† Formula: $\varepsilon=a+b$ log. D.
ε=Hydrogen over-potential.
a and b are constants depending on the experimental conditions.
D=Current density.



(*a*)—50 *mg Ni/l.* (*b*)—100 *mg Ni/l.* (*c*)—500 *mg Ni/l.*



(*d*)—1 *mg Sb/l.* (*e*)—10 *mg Sb/l.* (*f*)—20 *mg Sb/l.*



(*g*)—10 *mg Sb/l.* 0*g Gelatine*/100 *ccm.* (*h*)—10 *mg Sb/l.* 0·05*g Gelatine*/100 *ccm.* (*i*)—10 *mg Sb/l.* 0·2*g Gelatine*/100 *ccm.*

FIG. 4

skin. This property was also noticed under certain conditions with arsenic, aluminium and lead.

Table II. and graph Fig. 6 show how the critical current density is influenced by acidity, temperature and zinc concentration.

TABLE II.

Sulphuric acid in gms./100 c.cm.	Critical current density $\frac{A.}{m^2}$
10·1	30–40
18·5	35–40
30·6	About 13
39·3	„ 520

Cobalt cathodes, Gel. Nil.
Electrolyte 20° E., 8 g., Zn/100 c.cm.

EVALUATION OF RESULTS.

The following general conclusions are drawn from the authors' experiments :—

(1) The nobler metals are deposited before, or together with, zinc even when present in traces

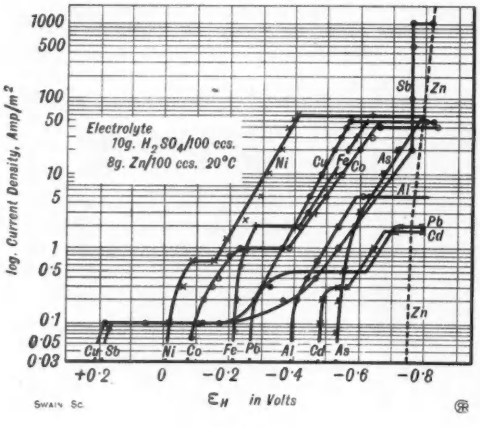


FIG. 5

only. The less noble metals can only be so deposited when present in high concentration.

(2) Zinc can only be deposited on the metals present as impurities when a critical current density, differing for each metal and varying with the depositing conditions, is exceeded.

(3) With constant current, the actual current density decreases as deposition progresses, because the surface area increases with the roughening of the deposit.

(4) Roughness of deposit tends to become exaggerated through stagnation of electrolyte in pits and depressions which causes a decrease in the zinc ions and an increase in hydrogen ions in the electrolyte layer immediately adjacent to the cathode.

(5) (3) and (4) act together to raise the critical current density, and when once the value falls below the critical point, zinc cannot be deposited on the impurity, but only on the aluminium cathode plate, or on zinc already deposited. This brings about a condition favourable to corrosion, the extent and intensity depending on the potential difference between the impurity and zinc and the number of places on which impurity is deposited.

(6) These considerations show that the equilibrium potential is not so important as the current density potential curve, and the hydrogen overpotential in the neighbourhood of the critical current density.

(7) Corrosion is increased by higher conductivity, as determined by the acidity and temperature of the electrolyte, because, for a given potential difference, a greater current passes.

(8) An increase in the concentration of zinc ions close to the cathode may be caused by corrosion, and this, by lowering the critical current density, favours the redeposition of zinc on an impurity. Such a deposit will, however, be spongy because the presence of hydrogen bubbles (which are the result of the corrosion) restricts the deposition to the continually changing boundaries of the bubbles.

CONCLUSIONS AS TO THE EFFECTS OF THE VARIOUS IMPURITIES TESTED.

Copper is deposited with zinc from very small concentrations. With increased concentration zinc is re-dissolved as soon as deposited, causing the formation of spongy zinc.

Cobalt acts similarly to copper.

Nickel acts somewhat differently. Its intrinsic potential is lower than that of copper, hence, in low

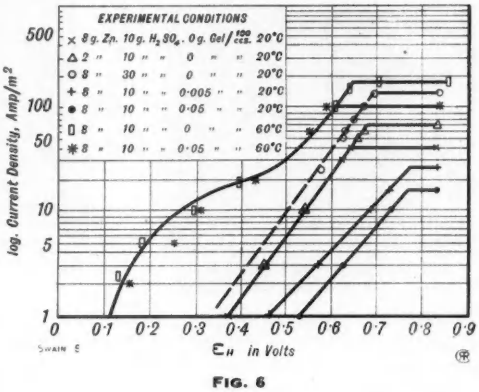


FIG. 6

concentration, less nickel is deposited than copper, and there are fewer points for corrosion to start. On the other hand, with high current densities nickel becomes nobler than copper and then the action spreads. This explains the characteristic appearance associated with nickel corrosion on cathodes.

Arsenic does not cause corrosion, but tends to cause nodular growths through the formation of protective coatings, apparently of a colloidal nature.

Antimony acts in the same way as arsenic, but to a greater degree, since it tends more readily to form protective films. There is little tendency toward corrosion on account of the small potential difference between antimony and zinc.

Cadmium favours nodular growth when present in high concentration, for a different reason. Zinc is more easily deposited on cadmium than on itself, so that immediately a trace of cadmium is deposited zinc is preferentially deposited on that spot and a nucleus for building up a nodule is provided.

Iron is only deposited in traces from concentrations as high as 5000 milligrammes per litre. It decreases

the current efficiency by being alternately reduced and oxidised at cathode and anode.

The authors express their intention of extending their work to include the investigation of the influence of impurities simultaneously present. The results obtained should be of considerable interest from a practical point of view, for, as the authors suggest, it is likely that these effects will not be merely additive.

Gases in Metals.

AT the New York meeting of the American Institute of Mining and Metallurgical Engineers a paper was presented on the above subject by V. H. Gottschalk and R. S. Dean which contained some interesting ideas. The authors reviewed the work of Sieverts and emphasised the need for the further study of the solubility of compound gases—particularly by the method used by Stubbs for sulphur dioxide and copper—in connection with the interpretation of the $\sqrt{P}$ law. They refer to "simple solubility" used to designate what is usually known as "physical solubility," which presumably occurs when such gases as oxygen, hydrogen, and nitrogen dissolve in water, and would exclude the phenomena observed when such gases as ammonia, carbon dioxide, or sulphur dioxide are dissolved. It also excludes all processes of an adsorptive nature.

Gottschalk and Dean make a computation of what is known as the "ideal solubility" of a gas in a hypothetical solvent having the properties of a molten metal. They follow the method given by Hildebrand,* which consists in first plotting log p against 1/T for the saturation pressures of the gases, then extrapolating beyond the critical temperature to the temperature required and secondly, in correcting for the internal pressure by the method given by Mortimer.† Results obtained by this method are given in Table I. for nitrogen and a number of

TABLE I.

Substance.	Internal pressure (H).	Ratio of solubility to ideal solubility.	Solubility of nitrogen per 100 gms. solvent.	
			c.c.(N.T.P.)	Temp. °C.
Octane	740	1·000	19·5	20
Water	37,700	0·020	2·49	20
Mercury	34,400	0·022	0·25	20
Silver	125,700	0·0059	0·018	727
Copper	233,100	0·0032	0·025	727
Nickel	279,700	0·0026	0·025	727
Iron	319,700	0·0023	0·023	727

liquids. It is not denied that the wide extrapolation used in obtaining this "ideal solubility" may give unreliable figures and the values for the internal pressures are not known with sufficient accuracy to give even a rough approximation for the solubility correction. It is considered that the solubilities for the metals which are given in column III. are much too large because, although the value obtained for the solubility of nitrogen in water (2·4 c.c.) is of the same order of magnitude as the observed value (1·5 c.c.) the figure calculated for the solubility of nitrogen in mercury is obviously very much too large. The cause of the discrepancy (in the case of the metals) is considered possibly to be their very high dielectric constant and it is concluded "that the simple solubility of gases in molten metals at higher temperatures, if not absolutely zero, is certainly less than the experimental error of modern precision laboratory methods." In confirmation of this view is cited the work of Steacie and Johnson, who found nitrogen to be insoluble in silver. Gottschalk and Dean consider that this one instance is quite sufficient to prove the point, as the "simple solubility" of gases in solvents is of the same order for all gases in one solvent.

The authors comment on the great lack of agreement obtained by different workers in recent determinations of the solubility of gases in metals. For example, Sieverts, Bircumshaw and Iwasé give respectively, for the solubility of hydrogen in tin at 800 deg., 0·00, 0·35, and 1·0 c.c. per 100 grammes of metal. Reduced to mass, the last two volumes are respectively 0·000031 and 0·000090 grammes of hydrogen in 100 grammes of tin. That these small amounts can be detected with any accuracy is, of course, due to the facility with which small volumes can be measured; also it happens that the solubility of most permanent gases in water at ordinary temperatures is of the same order of magnitude as the volumes absorbed by molten metals at high temperatures, and this coincidence, according to Gottschalk and Dean, has helped to obscure the fundamental difference between the two sets of phenomena.

It is pointed out that liquids of high internal pressure and great electrical conductivity might be expected to exhibit a considerable ionising power on solutes, and that the phenomena exhibited in the interaction of gases and molten metals could very likely be explained in terms of the electronic structure of gases and metals. The recent successes of the electronic theory of valency in explaining the structure of varying types of compound are recalled.

Some of the points raised in Gottschalk and Dean's paper are extremely interesting; nevertheless, many of the ideas put forward must be considered to be highly speculative.

Sulphur Printing.

WE have drawn attention from time to time to various developments in the technique of obtaining contact prints from steel sections in order to show segregation of sulphur, phosphorus, oxygen, &c. The original so-called "sulphur printing" method, due to Baumann, probably on account of its ease and simplicity, and the fact that its indications are now widely appreciated, remains the most popular means of demonstrating the distribution of impurities in a steel section. When prints of this kind are made the first impression obtained from a freshly prepared steel surface is always the best, and although two and possibly three further impressions can be obtained by more prolonged contact with further pieces of silver bromide paper, the sharpness and depth of the images deteriorates at each repetition. If, as is sometimes the case, a number of replicas of a sulphur print are required, then the only method of producing them which has hitherto been available has necessitated the taking of a full-size photograph of the

* Hildebrand, "Solubility," pp. 32–35. Monograph, American Chem. Soc. The Chemical Catalog Co., 1924.

† *Ibid*, pp. 113–116.

original Baumann print and the subsequent printing of replicas by the usual photographic methods.

In the issue of *Stahl und Eisen* for December 29th of last year, attention is called to the facilities which a new photographic treatment offers in this connection. The brief note relating to this matter appears over the names of H. Baars, A. Prill, and M. Werner. They call attention to the use of a new silver bromide transparent paper produced by Agfa. This can be treated exactly like ordinary silver bromide paper, and after soaking in 5 per cent. sulphuric acid an application to the steel surface gives a sulphur print of the usual kind. This method has the advantage of producing a transparency from which contact prints may be taken in any desired number on the usual photographic paper. These, if taken direct from the contact print transparency will, of course, be negatives, and it is possible that their interpretation in that form may not be quite so easy as that of the direct prints. This difficulty may, however, be avoided by first making a transparency negative by contact from the original transparency print, and printing subsequent replicas of the original from this negative. In that case the only difference between the direct print obtained by contact with the steel and the replica will be in the colour, unless one goes to the trouble of toning the photographic prints to a brownish tint resembling that of the original image. It seems likely that in cases where a large number of copies of sulphur prints are required this new material will prove of considerable convenience.

Copper-Cadmium Alloys.

THE equilibrium diagram of the alloys of copper and cadmium has been investigated by Jenkins and Hanson* using thermal and microscopic methods. The system has recently been subjected to analysis by X-ray methods by Owen and Pickup,† who confirm the earlier work and add some new facts to our knowledge of the alloys. A general survey of the system by the powder method of crystal analysis confirmed the existence of the four intermediate phases reported by Jenkins and Hanson; of these only one, the δ phase of Jenkins and Hanson's diagram yielded a spectrum which could be solved. The structure of this phase is cubic, having fifty-two atoms in the unit of side 9·596 Å, and has been studied in detail by Bradley and his collaborators.‡ It is structurally analogous to the γ phase of the copper-zinc alloys, and has a composition close to $Cu_5 Cd_8$. The other three phases, β with a copper content of 53·5 weight per cent. copper, γ containing 43·2 per cent. copper, and ε with 15·6 per cent. copper, yielded powder photographs which were not amenable to solution. These phases are evidently structurally complex. Owen and Pickup direct attention to the fact that this system of alloys differs from the systems Cu-Zn, Ag-Zn, and Ag-Cd in not possessing any phase of the simple body-centred cubic type characteristic of β brass, and they fail to detect the existence of the close-packed hexagonal phase found in these other systems.

* *J.*, Inst. Metals, Vol. 31, page 257 (1924).

† Proc., Roy. Soc., A Vol. 139, page 526 (1933).

‡ Proc., Roy. Soc., A Vol. 112, page 678 (1926); *Phil. Mag.*, Vol. 12, page 143 (1931).

The chief point of interest in Owen and Pickup's work is the determination of the limit of solubility of cadmium in copper at different temperatures. Jenkins and Hanson were unable to detect any change in the solid solubility of cadmium in copper and the solubility limit on their diagram was accordingly shown as a vertical straight line at a composition of approximately 97·3 per cent. by weight of copper. The X-ray evidence now put forward appears to prove definitely that the solubility of cadmium

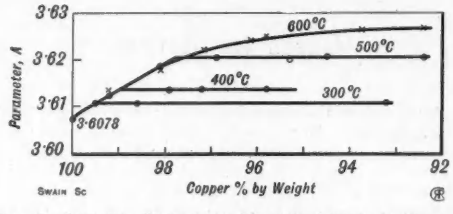


FIG. 1—COPPER-CADMIUM ALLOYS LUMP ANNEALED

increases from about 0·5 per cent. cadmium at 300 deg. Cent. to about 3 per cent. cadmium at 549 deg. Cent., the eutectic temperature. Owing to volatility of cadmium at comparatively low temperature, great care is necessary in the preparation of specimens. The authors have been at pains to develop a method of preparing their material which leads to consistent results. The cast alloy was annealed for a prolonged period (600 hours) and then the surface layer to a depth of at least 1 mm. was discarded.

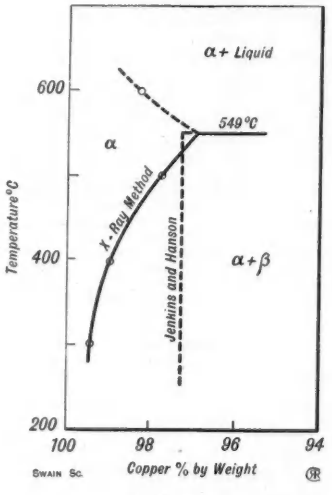


FIG. 2

Filings from the interior of the metal were then prepared for X-ray examinations by annealing at the required temperatures in evacuated pyrex tubes and quenching. Chemical analysis was carried out on the specimens actually used for the X-ray work. The results of the accurate X-ray photographs of a series of alloys quenched from different temperatures are shown in Fig. 1, taken from Owen and Pickup's paper. At each of the temperatures employed it will be seen that the final constant value

of the parameter of the α solid solution is different; this is positive evidence of a change of solid solubility with temperature. The suggested modification of Jenkins and Hanson's diagram is shown in Fig. 2. The change is small, but may be of importance, because a solubility decreasing with temperature is generally accompanied by age-hardening.

The curve in Fig. 1 corresponding to an annealing temperature of 600 deg. Cent. is of interest. According to Owen and Pickup the point where it diverges from the linear parameter-composition curve (about 98 per cent. copper) represents the composition of the solid phase in equilibrium with liquid at 600 deg. Cent., and they have shown this point on the solidus in Fig. 2. It is peculiar, however, that the parameter of the α phase should continue to increase with cadmium content beyond the point of intersection of the solubility limit and the eutectic at 549 deg. Cent. This limiting concentration, about 97 per cent. copper, should be the most highly concentrated alloy obtainable under equilibrium conditions, yet the parameter apparently continues to increase, though slowly, up to a composition of 95 per cent. copper. There is here a point that requires further investigation.

Perusal of this interesting paper would have been easier if it had been subjected to more careful revision before publication. The meaning of several sentences is obscure, and there is at least one numerical error (on p. 539) which might have been avoided; but, apart from this, the authors are to be congratulated on having produced a careful revision of that part of the diagram which is of technical importance.

Bismuth in Copper.

Sir,—In view of various developments which have recently taken place in the metallurgy of copper and brass, the effect of small proportions of bismuth upon the mechanical and other properties of these materials has assumed greater importance than ever before. Simultaneously, the development of various sources of copper which may contain more or less bismuth has rendered it supremely important for the manufacturer to be able to know with certainty the bismuth content of the metal he is employing.

Since the proportions of bismuth which have to be determined are very small, the actual estimation is an operation which presents considerable difficulties, and a careful examination of the whole position by the Technical Sub-Committee of the Fiscal Policy Committee of the Brass and Copper Industries has shown that there is generally a good deal of uncertainty in the assays which are made. Since the bismuth content affects the buying and selling of many thousands of tons of copper per annum, it is obviously essential that entirely sound and reliable results shall be obtained when analysing for this element, and in an endeavour to arrive at such a position the above-mentioned Technical Committee has thoroughly investigated the matter.

As a result of this examination, a set of principles has been enunciated by the Committee which they consider will, in the hands of competent analysts, produce reliable and reproducible figures. In making a statement of these principles the Committee does not wish it to be believed that it is excluding other possible methods, but wishes to affirm that in laying down certain rules it has produced a means whereby sound analytical results can be obtained.

In view of the exceedingly great importance of securing the most complete reliability in analysing for bismuth the Committee would be grateful if you would arrange to give publication to the document enclosed and also to this letter, which explains how it came into existence. It is hoped that by these means all those who are interested in this problem will have an opportunity of seeing and criticising these proposals with a view to the eventual perfection of this particular determination, and the Committee will be glad to receive from interested parties any comments or suggestions tending towards this result. These should be addressed to the Secretary, Mr. Lester Smith, c/o Squiers and Co., King's Court, 115, Colmore-row, Birmingham, England.

A. J. G. Smout, *Chairman*,
J. Lester Smith, *Secretary*,
Fiscal Policy Technical Sub-Committee
of the Brass and Copper Industries.

In dealing with this matter it has been considered desirable to enunciate those analytical principles which should be observed in making an analysis for bismuth, rather than to lay down details of chemical procedure. The intention is to provide a set of rules which, in the hands of competent analysts, will produce reliable results. Within the principles enunciated there is ample scope for variation in accordance with individual preference. It is not claimed necessarily that the methods which would follow from the given rules are the only ones which may give reliable results, but it is claimed that the principles set out below, if faithfully observed, will always yield reliable and reproducible values.

(1) The proportions of bismuth in question are too small to allow of satisfactory determination by gravimetric means. If a gravimetric estimation is attempted it is necessary to use a very large quantity of material and, as a result, the operations involved in the separation of the bismuth become too clumsy for the requisite accuracy to be obtained. Furthermore, the handling of the final precipitate presents marked difficulties in view of the small quantity which is present.

(2) The most satisfactory method of determining the bismuth is by colorimetric means and a suitable reaction for this purpose is that between bismuth sulphate and potassium iodide. This reaction releases bismuth tri-iodide, which dissolves in an excess of potassium iodide, producing a yellow solution.

(3) In opening out the copper, solution should be effected by nitric acid; 10 c.c. of nitric acid (Sp. Gr. 1·20) per gramme of copper is a suitable allowance. In the event of an insoluble residue being obtained this should be filtered off, ignited and fused with potassium bi-sulphate, the fusion dissolved in dilute sulphuric acid and added to the original filtrate.

(4) In order to ensure that the whole of the bismuth is precipitated during separation it is necessary to have present a sufficient quantity of another element to act as a collector. Of the various elements which might be employed, iron is the most satisfactory. In impure coppers there may be sufficient iron present to act as a collector, but in view of the uncertainty of this iron content it is preferable to make a specific addition of iron to the dissolved sample (0·25 gramme of ferrous ammonium sulphate per 10 grammes of sample is a satisfactory proportion).

(5) In precipitating the bismuth the caustic alkalies should be definitely avoided and an entirely satisfactory precipitant is ammonia.

(6) Re-precipitation of the mixed hydroxides of bismuth and iron is essential in order to avoid contamination of the bismuth solution finally obtained with copper.

(7) The complete precipitation of the bismuth requires some considerable time, and it is necessary to allow the solution, both for the initial precipitation and the re-precipitation of the bismuth to stand in a warm place for at least six hours.

(8) When the final precipitate of the mixed hydroxides of iron and bismuth, from which the copper has been completely removed, is re-dissolved, solution should be effected in sulphuric acid. The resulting solution should be neutralised, then brought to a condition of slight acidity, after which all the iron must be reduced to the ferrous condition. The reduction can be effected most conveniently by means of sulphurous acid.

(9) The final solution is matched against a blank solution which has been prepared by carrying through all the analytical operations as applied to the sample under assay, but to which no sample has been added. Into this resulting solution the standard bismuth solution (containing 0·0001 gramme bismuth per c.c.) is added until the colours match. The bismuth solution is best prepared by dissolving 0·1 gramme of metallic bismuth in 20 c.c. concentrated sulphuric acid and making up to a litre.

(10) In the final solutions the acidity should be approximately 2 per cent. by volume and the amount of potassium iodide added should be adequate but not excessive. A suitable proportion is about 10 c.c. of a 2 per cent. solution. The aliquot proportion taken of the solution under assay should be such that not more than 4 c.c. of the standard bismuth solution should be required.

For proportions less than 0·002 per cent. of bismuth the methods based on the above principles may not be trustworthy. Methods for the determination of these very small proportions are at present under investigation.

The Standardisation of the Scleroscope Test for Specification Use.*

By R. GENDERS.

THE scleroscope hardness test, although limited as regards accuracy and sensitivity, has been widely adopted as a rapid means of determining the hardness of metals. Its rapidity renders it useful for controlling, within set limits, the regularity of large numbers of the same kind of product, particularly in the manufacture of certain classes of cold-worked non-ferrous metals and alloys, and the test has been frequently included in private specifications and those of the Government Services. In the past, certain difficulties have been experienced in the use of the scleroscope for acceptance tests on soft metals, and investigatory work has been carried out at the Research Department, Woolwich, with the object of improving the reliability of the test. The resulting modification has been used as a standard by Government Departments in this country and abroad, and has now been adopted by the British Standards Institution in a number of Standard Specifications dealing with brass and copper, in which the scleroscope test is included as an alternative to the ball hardness test. The following explanatory notes may therefore assist users of the scleroscope test in view of the fact that the instrument itself is proprietary, and has been standardised independently for the specification testing of the non-ferrous metals.

First described by A. F. Shore in 1907, the scleroscope is now so well known that a description in detail is unnecessary. The principle of the test is the measurement on an arbitrary scale of the rebound of a small weight (or " hammer ") dropped vertically on the surface of the test specimen, the area of impact being sufficiently small to cause some deformation. In common with many other widely used methods of testing materials, the scleroscope test is quite empirical in character. The conditions vary considerably according to the properties of the specimen tested, and the scleroscope hardness number is consequently not to be regarded as an actual measurement of any particular single property of the material. It is generally accepted that the property which determines the scleroscope reading is the coefficient of restitution between the material tested and the hammer under conditions where permanent deformation is produced.

For practical purposes, however, and within limits, the scleroscope value can be correlated with other properties of a material, and by its use the uniformity of, for example, the " temper " of cold rolled metals can be satisfactorily gauged. Certain precautions are necessary in the testing of thin strip or light specimens. These have been dealt with in published papers by Blenkarn* and by Tritton.†

Two types of " hammer " are used in the scleroscope. That known as the " Universal " hammer has a diamond nose inserted in the striking point, while the " magnifier " hammer is of solid steel with a blunt conical shaped striking point. The universal hammer, owing to the hardness of the diamond nose, produces a greater degree of deformation of the specimen under test, and the rebound is consequently lower than that of the magnifier hammer for the same material. The main advantages of the universal hammer are its immunity from wear and the fact that there is little variation in the results given by different instruments. For relatively hard materials therefore the diamond-pointed hammer should be generally used. For tests on softer materials, such as most non-ferrous alloys, the diamond hammer gives undesirably low readings, and if appreciable sensitivity is required, the magnifier hammer must be used. With this type of hammer, however, continued use produces wear ; the nose of the hammer becomes flattened, and the rebound tends to increase, giving high results. A further more serious objection is the wide difference in results which has been frequently found between different instruments, and for this reason the magnifier hammer has been formerly little used.

The suitability of the test for certain types of routine testing, and the necessity for the maximum degree of sensitivity, led to the investigation of the possibilities of standardising the scleroscopes used at the War Office inspecting stations in order to ensure strict comparability of readings.

It was found that the lack of agreement between magnifier hammer readings of different scleroscopes was due to slight variations in contour of the striking

* Communication from the Research Department, Woolwich.

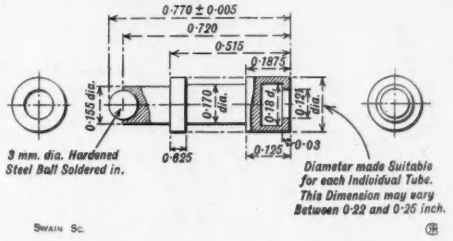
* *Journal*, Inst. Met., 1921, 25, 345–346.

† *Journal*, Inst. Met., 1921, 26, 261–270.

portion of the hammer nose, and a new form of hammer was accordingly designed in which constant and definite contour of the nose was ensured by employing a hardened steel ball soldered into a hemispherical socket at the lower end of the hammer. The type of ball was that ordinarily supplied for use in ball bearings; a high degree of accuracy of dimensions can be relied upon. The 3 mm. ball hammer was selected as standard for use by the Service Departments, and has been adopted by the British Standards Institution, in addition to the diamond hammer. The readings are similar to those of the majority of magnifier hammers, providing adequate sensitivity for tests on most industrial metals. With the introduction of the ball hammer it has been found possible to obtain concordant and comparable results in all types of material over the entire range of hardness dealt with in practice.

The drawing given below shows the dimensions of the 3 mm. ball hammer universally suitable for the ordinary visual scleroscope instrument.

Investigation has shown that slight variations of diameter and weight of the hammer necessitated by



STANDARD 3 M/M BALL SCLEROSCOPE HAMMER

differences in the bores of the glass tubes of different instruments are without sensible effect on the results of the test. The method of preparing the ball hammer and the results of the initial investigatory work carried out at the Research Department, Woolwich, are described in a paper by R. Genders.*

The standardisation of instruments for use in the War Office inspecting stations is accomplished by retaining a scleroscope specially verified for accuracy by the makers, and fitted with the 3 mm. ball hammer, for the standardisation of test blocks. Certain test blocks are reserved for the periodical checking of this instrument.

Glass tubes are obtained from the makers to fit hammers of 0·240in. diameter, which is the diameter adopted as the standard at the Research Department, Woolwich.

The examination is carried out by testing them in a scleroscope, using calibrated blocks and a 3 mm. ball hammer which has been prepared and tested as described below. Tubes supplied to take 0·240in. diameter hammers have usually given satisfactory readings. Tubes which do not give a correct nature of fall and return of the hammer are rejected. No other examination is made for uniformity of tube diameter.

The body of the hammer is made of mild steel. After fitting the hard steel ball, each hammer is tested in a scleroscope, preferably that in which it is to be used, and is hand fitted to ensure its being easily gripped and released by the scissors in the head of the instrument. The diameter is standardised for all new work at 0·240in.

For fixing the ball, a small flat piece of solder is placed in the ball socket, damped with zinc chloride flux, and the ball placed over. The end of the hammer is heated with a small blow-pipe flame, and pressure is applied on the ball at the same time. Care must be taken that the flame is applied only to the stem of the hammer, so that the ball is not unduly heated and softened. As soon as the ball sinks into position, showing that the solder has melted, the flame is removed, the hammer cooled with a damp cloth, and the excess solder trimmed off with a knife.

The ball hammers are tested by 6–12 readings on each of three blocks—soft, medium, and hard. New hammers or hammers refitted with new balls invariably give correct readings.

Steel for calibrating blocks is obtained in the form of normalised bars of crucible carbon steel, 6ft. to 10ft. long and 1½in. diameter. The bars are cut into 3in. lengths, ¼in. is turned off, and each piece is machined to hexagon section. Machine marks are finally removed on emery paper. The hardness of the block is tested against a calibrated block of similar hardness, using the instrument retained as a standard at the Research Department, Woolwich. Six determinations are made on each face of each block. From these thirty-six determinations the 3 mm. ball reading for the block is obtained. Blocks giving many readings more than one division on either side of the mean are discarded. Each block is calibrated similarly for "Universal" hardness by using the diamond pointed hammer originally supplied with the scleroscope adopted as a standard.

Brass blocks have been found unsuitable for reference standards. Stainless steels may ultimately be found to be the most useful materials for this purpose.

All blocks are stamped at one end with the 3 mm. ball and universal hardness numbers, and at the other end with an identification mark. A card index record is kept of all blocks and instruments standardised.

In industrial use, the 3 mm. ball hammer, although constituting in itself a standard, should be suitably calibrated at intervals on test blocks and compared with a similar hammer reserved for the purpose. Wear of the ball is likely to be slow with all but very hard materials, but inevitably occurs. A worn ball can readily be distinguished visually by the appearance of a dull spot on the bright surface of the ball at the point of impact. The ball can be simply replaced, and this should be done when an appreciable plus error is shown on calibration.

Under these conditions the use of the 3 mm. ball hammer may be relied upon to ensure that any two scleroscopes will give equal results on the same material, and should avoid disputes between maker and user such as have frequently occurred when the ordinary magnifier hammer was used.

The new type of dial-reading scleroscope has not been standardised. It is understood, however, that tests have been made which have shown that, with a 3 mm. ball fitted in the hammer, the readings given by the instrument agree with those given by the ordinary type.

* *Journal*, Inst. Met., 1923, 29, 445.

Graphite Oxidation.

By J. G. PEARCE, M.Sc., M.I.E.E.

THERE are various directions in which the conventional conception of cast iron as a steel matrix broken by graphite flakes is unsatisfactory. One of these is disclosed in considering various difficulties arising in the welding and in the vitreous enamelling of cast iron. Repeatedly in technical articles and papers it is suggested or implied that the graphite is the origin of these difficulties, since it furnishes the only difference between cast iron and steel, which is comparatively easily treated in these processes. The author has recently drawn attention to the possibility of error in this view in a paper to the Institution of Welding Engineers on metallurgical considerations in the welding of cast iron and some ferrous alloys. As far as the graphite *per se* is concerned, the author believes that cast iron should be as readily welded as steel. The usual presumption is that graphite is oxidised to carbon monoxide and carbon dioxide, and that the resulting gases are responsible for the defects so frequently met in both of the above-mentioned processes and shown by holes or pits.

Graphite is well-known to be an extremely stable form of carbon, more stable in some respects than the diamond. If it were primarily responsible for the trouble it would be expected that irons containing fine graphite would be more susceptible than those with coarse graphite, but this is not borne out by experience in the above-mentioned processes. In a series of heat-resisting irons developed by the British Cast Iron Research Association, known as "silal" irons, the graphite is in an extremely fine state of division. If graphite is oxidised, irons with fine graphite would be less resistant than those having coarser graphite, assuming that other things were equal. Actually the reverse is the case, and the finer the graphite structure the greater the resistance. The greater readiness with which fine graphite may be presumed to dissolve is more than counteracted by the greater ease of penetration of coarse flake cavities by the gases, leading to oxidation of the iron itself.

The practice of annealing white graphite-free iron by heating in an oxidising ore, thus yielding a highly oxidising atmosphere, for the purpose of making malleable castings by the whiteheart process affords another illustration. This process is carried out at a comparatively high temperature, 900 deg. to 1000 deg. Cent. It is generally accepted that the process of softening proceeds by the breakdown of the carbide or cementite in the white iron. The reactions are given by Hatfield :—

$$2\,Fe_3C + 2\,CO_2 = 3\,Fe_2 + 4\,CO$$
$$2\,CO + O_2 = 2\,CO_2$$
$$2\,CO_2 + 2\,Fe_3C = 3\,Fe_2 + 4\,CO \ldots \text{continuously.}$$

The process does not proceed by way of the reactions :—

$$Fe_3C = Fe_3 + C$$
$$C + CO_2 = 2\,CO$$
$$2\,CO + O_2 = 2\,CO_2$$
$$C + CO_2 = 2\,CO \ldots \text{continuously,}$$

which would represent the simple oxidation of graphite.

This process, in fact, provides the commonest example of the deposition of temper carbon, the finest form of graphite, and, on the basis commonly assumed, the most readily oxidisable form. When a malleable casting prior to annealing happens to contain primary graphite, that is, to be mottled or slightly grey, this graphite usually increases in size during the annealing process, and tends to yield a mechanically inferior structure. It must be admitted that temper carbon is seldom found near the oxidised face of the metal.

The question has recently been considered independently by Mr. G. L. Bailey in a paper on non-ferrous strip ingot moulds, in which ingots required for special purposes were rendered defective by "blowing" from the cast iron mould. The possibility of this being due to loss of graphite was considered, but tests showed that the amount and state of division of the graphite in the moulds did not influence their behaviour as regards blowing. Tests were then made to see whether the gas responsible for the blowing was due to a reaction between the carbide present in the mould and a superficial oxide film, and they confirmed the fact that decarburisation occurs at the expense of the carbide and not of the graphite. This action was found to proceed at 700 deg. to 800 deg. Cent.

While it may be regarded as immaterial whether the trouble arises from carbide or graphite in processes carried out at temperatures at which the graphite may go into solution as carbide, it is important that the conception of what takes place should be clear. Graphite, of course, in the ordinary way does not completely fill its cavity, because it shrinks in the cooling process, so that air must be present in the cavity. This is not normally observed in micro-structures because the polishing material fills the cavities and reveals the size of the cavity itself.

In the enamelling process the above considerations suggest the importance of the annealing of the metal either by a preliminary treatment or during the enamelling process itself, for this tends to break down the carbide of the pearlite completely to ferrite and graphite. It is also well known that steels containing more than 0·3 per cent. of carbon are difficult to weld. Graphite or no graphite, cast irons usually contain more than this percentage of combined carbon and would on this account be expected to cause difficulties due to gas evolution and entrapped gases. The austenitic cast irons, by virtue of their austenitic structure, slight ductility, and of their resistance to oxidation, are much easier to weld. In enamelled cast iron there is no evidence of loss of graphite at the face.

The recognition of carbide as the source of gas formation under oxidising conditions has clarified many of the difficulties created by the view that the graphite itself is the cause. The fact that white iron can be welded or enamelled has to be considered in the light of the fact that white iron is usually low in silicon, or is otherwise stabilised, as by chromium, and hence has a relatively stable carbide, strong enough to resist breakdown in processes the heating period of which is comparatively short.